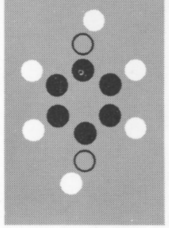
7



Chemistry of Development

Development is the method of making visible by using special solutions called "developers" the invisible latent image formed during exposure. How do these chemicals react in the developer in the presence of the latent image to make it visible?

• Development is actually a chemical reduction in which the exposed silver halides are reduced to metallic silver. In other words, the developer somehow causes the following reaction to take place:

$$\left.\begin{array}{l}\text{Ag Cl}\\ \text{Ag Br}\\ \text{Ag I}\end{array}\right\} \text{Ag (metallic silver)}$$

Chemical reducers were defined years ago as substances which have an affinity for oxygen and can liberate metals from their salts. For example, if hydrogen gas is passed through a heated tube containing black copper oxide, it will combine with the oxygen to form water and leave metallic copper in the tube. This reaction, written in chemical language, illustrates the use of hydrogen as a reducing agent, and its affinity for oxygen:

$$CuO + H_2 = Cu + H_2O$$

As the investigation of chemical reactions progressed, it was observed that chemical reductions occurred which did not involve hydrogen or oxygen. These reductions are the result of a change in the electrical relationships between atoms.

In Chapter V, ionization was described as the separation or splitting of a chemical in solution into positive and negative ions, e.g.,

$$NaCl = Na^+ + Cl^-$$

These ions are actually atoms of sodium and chlorine that are not neutral with respect to electric charge. According to modern atomic theory, all neutral atoms have an equal number of positive and negative electric charges. Since the sodium ion has an excess positive charge, the atom must have lost one negative charge, known as an "electron." The sodium has been oxidized. If, in some way, the excess positive charge on the sodium could be neutralized by acceptance of an electron, the sodium ion would be reduced to metallic sodium, i.e.,

$$Na^+ + \text{e (electron)} \longrightarrow \text{Na (metallic sodium)}$$

During photographic development, the emulsion is immersed in developer solution, and even though the silver halides are highly insoluble, a very small amount does dissolve and ionize to produce silver and chloride ions:

$$AgCl = Ag^+ + Cl^-$$

Since development is a chemical reduction, the reaction can be represented by the following equation:

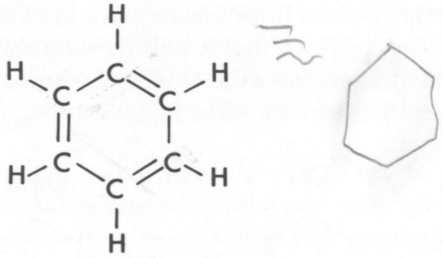
$$Ag^+ + e \longrightarrow \text{Ag (metallic silver)}$$

Once this reaction has started, more and more of the exposed silver halides ionize and are reduced until all of the exposed halide is converted to metallic silver. However, no simple equation can be written to explain the exact chemical steps involved in development with practical developing solutions. Actually, there are several different chemical reactions occurring at the same time and the chemistry is very complex.

DEVELOPING AGENTS

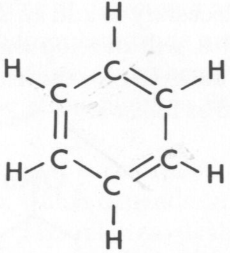
These agents are special organic chemicals which have the ability, when incorporated in a developer solution, to develop the exposed silver halides without affecting the unexposed halides. They are reducing agents which provide the electrons required to reduce silver ions to metallic silver.

The most commonly used developing agents are all related chemically to benzene, which has the formula C_6H_6. Organic chemicals are usually represented by *structural* formulas which indicate the relative positions in space of the atoms in the molecule. Benzene is represented by the following structural formula:

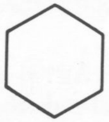


which shows that there are six carbon atoms in a ring, with one hydrogen atom attached to each carbon atom. Since this particular arrangement of six carbon atoms forms a basic unit or building block in a

Snapshot
know how

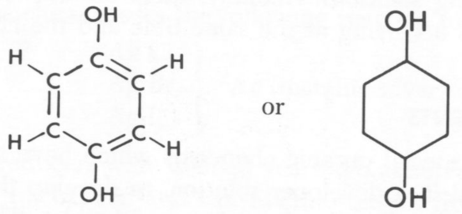


very large number of compounds, it is generally represented by the simplified symbol:



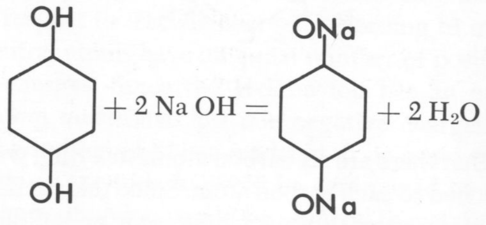
Each of the angles of this hexagon represents one of the six carbon atoms and its attached hydrogen atom.

By chemical reactions, small or large groups of atoms can be substituted for one or more of the hydrogen atoms. Thus, hydroquinone has the structure:

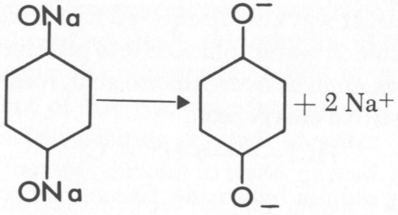


In reading the simplified symbol, it is understood that the two OH groups have replaced two of the hydrogen atoms, but that the other four hydrogen atoms are still in place at the four plain angles. The OH groups which have replaced two of the six hydrogens are called "hydroxyl" groups. Other commonly used developing agents are Kodak Elon Developing Agent, para-aminophenol, and paraphenylenediamine.

Generally, organic developing agents will not develop a silver image by themselves. It is necessary to add an activator to condition the developing agent so that it will develop the exposed silver halides. Using hydroquinone as an example, the effect of the activator, an alkali, can be represented as follows:



The sodium hydroxide reacts with the hydroquinone to form the sodium salt of the developing agent. This salt, being in a water solution, ionizes or dissociates in the same manner as sodium chloride or table salt –



The negative ion has two excess negative electric charges or electrons. It can give up these electrons to the silver ions formed from the silver halide, and this allows the reaction,

$$Ag^+ + e \longrightarrow Ag$$

or the reduction of the silver ions to metallic silver. *It must be remembered that this represents the end result of several chemical reactions.* However, it provides some idea of how the silver image is formed in the developer.

ACTIVATORS

The following alkalies are most commonly used as activators in photographic developers:

Sodium hydroxide, $NaOH$
Sodium carbonate, Na_2CO_3
Kodalk Balanced Alkali
Borax

These are listed in the order of decreasing activity, which means that developers containing sodium hydroxide are much more active than those containing borax. A given amount of image silver will be formed in much less time in the highly active developers than in the low-activity developers.

The activity of a developer is controlled, to a large extent, by the alkalinity of the solution, which depends on the particular alkali and the quantity of it used. The relative alkalinities of developers are generally indicated by pH values. The pH of a developer solution is affected by several of the chemicals used in the solution, but is determined primarily by the characteristics of the alkali employed. What is meant by the pH of a solution?

Two interesting developments in the early days of chemistry led to the introduction of the pH concept. Acids and bases (or alkalies) were first recognized by the fact that acids turned litmus paper* red and bases turned it blue. It was also discovered that acids, bases, and salts ionized or dissociated in water solutions into positively and negatively charged ions. Acids, such as hydrochloric acid, formed hydrogen ions having a single positive charge, e.g.,

$$HCl \longrightarrow H^+ + Cl^-$$

and bases, such as sodium hydroxide, formed hydroxyl ions having a single negative charge, e.g.,

$$NaOH \longrightarrow Na^+ + OH^-$$

It was concluded that the changes in the color of litmus paper were produced by the hydrogen or hydroxyl ions present in the solution. While litmus paper can show whether there are more or less hydrogen ions than hydroxyl ions present it soon became evident that a method was needed for determining the quantity or concentration of the hydrogen or hydroxyl ions present.

Ordinary water can be written chemically as HOH. It contains both hydrogen ion and the hydroxyl ion in equal concentrations:

$$HOH \longrightarrow H^+ + OH^-$$

But water does not ionize as readily as acids, bases, and salts. In fact, the electrical conductivity of pure water is so very low that it indicates that the degree of dissociation or ionization is so small that ordinarily it might be considered negligible. The fact that water does ionize slightly, however, can be used as a basis for the determination of acidity or alkalinity in water solutions. This can be done by using a relationship discovered between the concentrations of hydrogen and hydroxyl ions. The product obtained by multiplying together the numerical values of the two concentrations is a constant which can be expressed as follows:

$$[H^+] \times [OH^-] = K$$

This means that the product of the concentrations is always the same in any water solution, and that the concentration of one ion can be calculated from this relationship when the concentration of the other ion has been determined by analysis. For instance, in pure water the concentrations of hydrogen and hydroxyl ions are equal and are 0.0000001 when expressed in gram mols per liter. Thus, the value of K is

$$0.0000001 \times 0.0000001 = 0.00000000000001$$

In a solution of a weak acid, if the hydrogen-ion concentration is 0.00001, the hydroxyl-ion concentration would be 0.000000001; while, with a moderately strong alkali, if the hydroxyl-ion concentration is 0.0001, the hydrogen-ion concentration will be 0.0000000001. In all cases, the product of the two concentrations is 0.00000000000001. This is called the "dissociation constant of water."

It is apparent that it is difficult to write, or read, numbers like these, but very often they are written for convenience as factors of appropriate powers of 10. Consider the numbers in the following table and their simplified expression in exponential form:

$$100 = 1.0 \times 10^{2}$$
$$10 = 1.0 \times 10^{1}$$
$$1 = 1.0$$
$$0.1 = 1.0 \times 10^{-1}$$
$$.01 = 1.0 \times 10^{-2}$$
$$.001 = 1.0 \times 10^{-3}$$
$$.0001 = 1.0 \times 10^{-4}$$
$$.00001 = 1.0 \times 10^{-5}$$
$$.000001 = 1.0 \times 10^{-6}$$
$$.0000001 = 1.0 \times 10^{-7}$$

Thus, the value of K stated as 0.00000000000001 can be written as 1.0×10^{-14}, and the relationship between the hydrogen- and hydroxyl-ions in pure water as

$$[H^+] \times [OH^-] = K = 1.0 \times 10^{-14}$$

It can be assumed that pure water is neutral, and therefore that all neutral solutions will have the same hydrogen-ion concentration as pure water, or 1.0×10^{-7}.

In an acid solution there will be a higher concentration of hydrogen-ion than of hydroxyl-ion, and in a very strongly acid solution the actual value may approach 1.0×10^{-1}. On the other hand, in an alkaline solution the hydrogen-ion concentration decreases with respect to its concentration in pure water and approaches the value 1.0×10^{-14} as the solution becomes extremely alkaline. A decrease in the concentration of hydrogen-ions can be used to express an increase in hydroxyl-ions.

In practice, it has been found most satisfactory to determine the concentration of the hydrogen-ion, whether the solution is acid, neutral, or alkaline. But it was necessary to simplify the method of ex-

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**Litmus paper is an absorbent paper impregnated with a special organic compound capable of changing color in acid and basic solutions.*

pressing the hydrogen-ion concentration before it was widely accepted. Sorenson made the first simplification by suggesting that the exponents only be used, without their negative sign, e.g., 1.0 x 10^{-14} could be written as 14, and he called these figures "pH values." As a result, the following pH scale came into being.

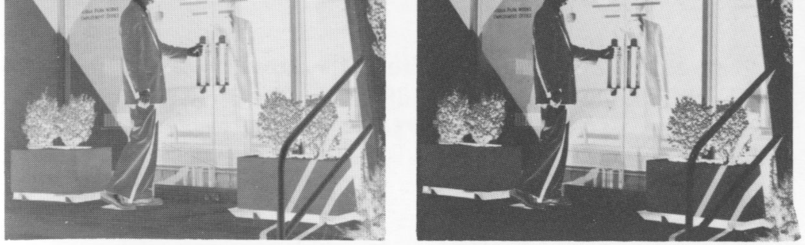
pH
14
13
12
11 alkalinity
10
9
8

7 } neutral

6
5
4
3 acidity
2
1

With suitable equipment, such as pH meters, this scale permits the determination of the number of times the acidity or alkalinity exceeds that of pure water. Since the pH scale consists of the exponents in the expression of hydrogen-ion concentration, the actual hydrogen-ion concentrations represented by successive numbers in the scale are related to each other by a factor of 10. For example, in the acid range, the concentration of acid increases as the pH value becomes smaller. A solution at pH = 5.0 contains 10 times more free hydrogen-ion than one at pH = 6.0, while a solution at pH 4.0 contains 100 times more than one at pH 6.0. Similarly, a solution at pH 10.0 contains 100 times more hydroxyl ion than one at pH 8.0, and so on.

As stated before, the alkali used in a developer controls its activity or the rate at which it develops the silver image. This effect is related primarily to the pH value produced in the developer solution. Developers with sodium hydroxide have a pH of approximately 12.0, and are extremely active; those with sodium carbonate have a pH of about 10.2 and are quite active; those with Kodalk Balanced Alkali have a pH of about 9.8 to 10 and have medium activity; and those with borax have a pH of about 8.5 to 9.0, with correspondingly low activity and long development time.



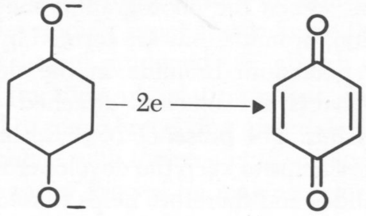
These negatives, exposed identically, were developed for the same times in Kodak Developer D-76 with normal pH of 8.6 (left) and pH adjusted to 9.5 (right). Note the increase in density and contrast produced by the more active developer.

Many materials that are ionized in solution exert a "buffer action," which means that they tend to resist or retard any change in the pH value of the solution. Thus, considerable quantities of acid or alkali can be added to a buffered solution, or the solution can be diluted, with only a very gradual change in pH value. The alkalies used in photographic developers are selected to provide buffering action at the desired pH levels. It is important that the developer maintain its characteristics while a considerable quantity of exposed photographic emulsion is processed in it; otherwise, the developer would not be very practical to use.

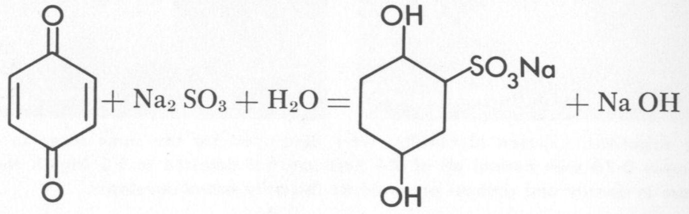
PRESERVATIVE

If a developing agent is dissolved in water, the solution will turn brown because of the breakdown of the developing agent by the action of the air (oxidation). When alkali is added to the solution, the breakdown takes place much more rapidly. Therefore, a preservative, usually sodium sulfite, is added to developer solutions to prevent this oxidation and thereby keep the solutions clear.

The sodium sulfite reacts with the oxidation products of the developing agent as fast as they are formed. Using the same example as on page 47, hydroquinone, the reactions may be written as follows. When the electrons of the negatively charged developing-agent ion are removed, quinone is formed:



Quinone reacts with sodium sulfite in the presence of water to form colorless sodium hydroquinone sulfonate and sodium hydroxide:



This is a very simplified representation of what actually happens, because other organic chemicals may be formed during oxidation of the developing agent and different ones are formed with the various developing agents. Generally, the sulfite salts formed play no part in the development, but there are some which are themselves developing agents and therefore contribute to the subsequent development.

The preservative action of the sulfite is its ability to prevent the developing agent in alkaline solution from being attacked by the oxygen in the air. If quinone, for example, were allowed to form in the developer solution, it would speed up the oxidation reaction. A chemical which speeds up reactions is known as a "catalyst." The sulfite prevents the accumulation of such a catalyst.

RESTRAINER

Potassium bromide is commonly used in development to restrain the formation of chemical fog, which is silver produced by action of the developer on unexposed silver halide. The bromide also assists in producing more uniform development. Although the addition of potassium bromide to a photographic developer may affect the rate of development of the image, it usually depresses the rate of fog formation to a greater degree than the rate of development. As a result, more efficient development is obtained. The chemical action of potassium bromide is quite complex and cannot be fully explained without considering in detail the proposed theories of photographic development. However, the general course of the action seems to be somewhat as follows. When the photographic material is placed in the developer solution, bromide ions are formed by the ionization or dissociation of the potassium bromide in the developer solution. These ions adsorb—that is, are somehow attached—to the surfaces of the silver halide crystals. The presence of these bromide ions (Br^-) on the crystal surfaces helps to keep the developer from attacking the unexposed silver halides and therefore helps to retard fog formation.

8

Chemistry of Color Development

In the development reaction, when the exposed silver halide is reduced to metallic silver, the developing agent is oxidized. The compounds formed by this oxidation are quite reactive and can be used to form color images.

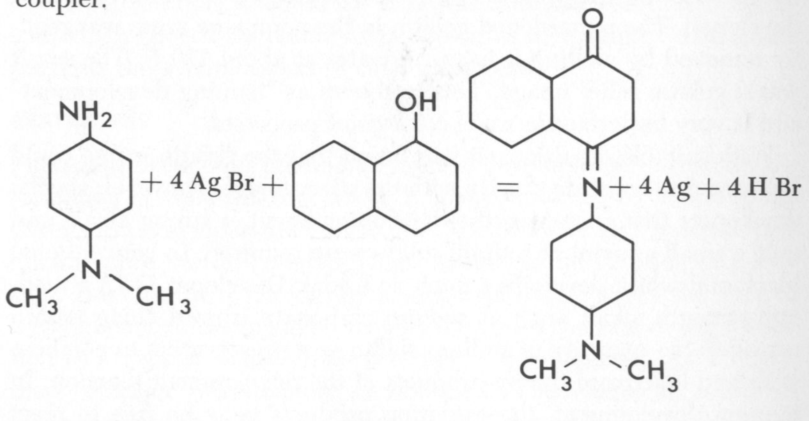
• It was observed as early as 1879 that some photographic developing agents produced a hardened gelatin image during the development of the silver image in a photographic emulsion. The gelatin image coincided with the developed silver image, and the thickness of gelatin hardened in the process was proportional to the amount of silver developed. The unhardened gelatin in the nonimage areas was readily removed by melting it in warm water at about 120 F. The result was a gelatin relief image. This is known as "tanning development" and is very important in some color-print processes.

With suitable emulsions, it was found that the gelatin image could be formed to coincide exactly with the silver image. However, special developers that contained the developing agent, a strong alkali, and only a small amount of sodium sulfite were required. In conventional black-and-white developers, such as Kodak Developer D-72 a medium-strength alkali, such as sodium carbonate is used along with a considerable quantity of sodium sulfite as a preservative to combine with and inactivate the by-products of the development reaction. In tanning development, the oxidation products must be free to react with and harden the gelatin, and the sulfite therefore must be left out or used in very small quantity. A very strong alkali, such as sodium hydroxide, is used to provide solutions of high pH to accelerate the oxidation of the developing agent and increase the hardening action. The gelatin relief image produced can absorb dye from a bath in proportion to the thickness of gelatin present, and the absorbed dye can be transferred to special receiving materials by bringing the dyed relief into close contact with the receiving surface. This is the basis of the Kodak Dye Transfer Process for making color prints on paper.

COLOR DEVELOPERS

The oxidation by-products of the basic development reaction can be used in various ways. For instance, under suitable conditions they can combine with certain other organic compounds to form colored dyes.

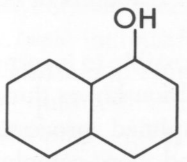
The dyes are formed as the result of a coupling reaction between the developer oxidation products and special dye formers, called "couplers," added to the system. Fortunately for the simplification of practical color processes, one developing agent can be used with different couplers to form dyes of the various colors needed. The color of the dye that is formed during color development is dependent on the chemical structure of the coupler. It is sufficient in this discussion to state that part of the coupler molecule is the color-forming part which determines the color of the dye formed, while the remaining part of the molecule affects the solubility of the coupler and its ability to diffuse or penetrate the emulsion layer. Both the coupler and the developer affect the solubility and the stability of the dye formed. The reaction is illustrated below with dimethyl-para-phenylenediamine as the developing agent and alpha-naphthol as a blue coupler.



dimethyl-para-phenylenediamine **alpha-naphthol** **indo-phenol blue**

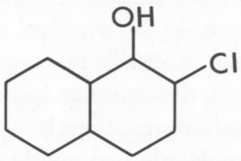
SELECTION OF COUPLERS

In any group of dye couplers, such as those producing blue or cyan dyes, small changes in the structure of a coupler molecule can cause a change in the color. For example, if chlorine is added to the alpha-naphthol coupler molecule, a different shade of blue dye is formed when it reacts with the oxidation by-product of the developing agent. The formulas for the two couplers are:



alpha-naphthol

and



chloro-alpha naphthol

Dye solutions absorb different wavelengths of light according to the color of the dye, and measurements of this absorption show the differences in the colors of dyes. The dye images formed in a color film with the two couplers alpha-naphthol and chloro-alpha-naphthol have their maximum absorptions at wavelengths of 630 $m\mu$ and 654 $m\mu$, respectively. By proper choice of the coupler, it is theoretically possible to produce any desired color. This is important in color photography because it makes possible the selection of the best combination of yellow, magenta, and cyan dyes to produce good color pictures.

In color development, silver is formed (in a given emulsion) in proportion to the exposure of the silver halides, and simultaneously the oxidation product of the developing agent reacts with the dye coupler to give a color image proportional to the silver image. Therefore, during color development there is formed an image which consists of silver and dye produced in proportion to the original exposure.

The requirements for a practical color-development system include: formation of an insoluble dye that will remain in the film; the choice of couplers to produce the proper color; dyes with good stability against fading; and developing agents that are not excessively toxic. Research has provided compounds that satisfy these requirements quite well for all practical purposes. There are two general types of color-development processes distinguished by the method of using the dye couplers, namely: (a) those which require the use of couplers in the color-developer solutions and (b) those which have the dye couplers incorporated in the emulsion layers.

The first commercially successful three-color dye-coupling reversal process was the Kodachrome Process. It consists essentially of three separate emulsion layers containing silver halides, with each layer sensitized differently to respond in exposure to specific parts of the visible spectrum. Each of the three complementary dyes — yellow, magenta, and cyan – is formed in its respective layer in three successive color developers containing appropriate developing agents and couplers. This means that the chemical reactions in each color developer must be confined to a single layer.

However, scientific research has made it possible to incorporate the appropriate dye coupler in each of the emulsion layers during product manufacture, thereby permitting simplified processing. The coupler molecules are made much larger and more complex so that they cannot wander away from their location in the emulsion layer, but their ability to react with oxidation by-products of the developing agent is not impaired. Kodak Ektachrome Film is a color product of this type. The number of processing steps is reduced because only one color developer is required. The developer reacts with the dye coupler in each emulsion layer in proportion to the silver image formed in that layer. This simplification of the color process has made it possible for the individual photographer or commercial laboratory to process color films.

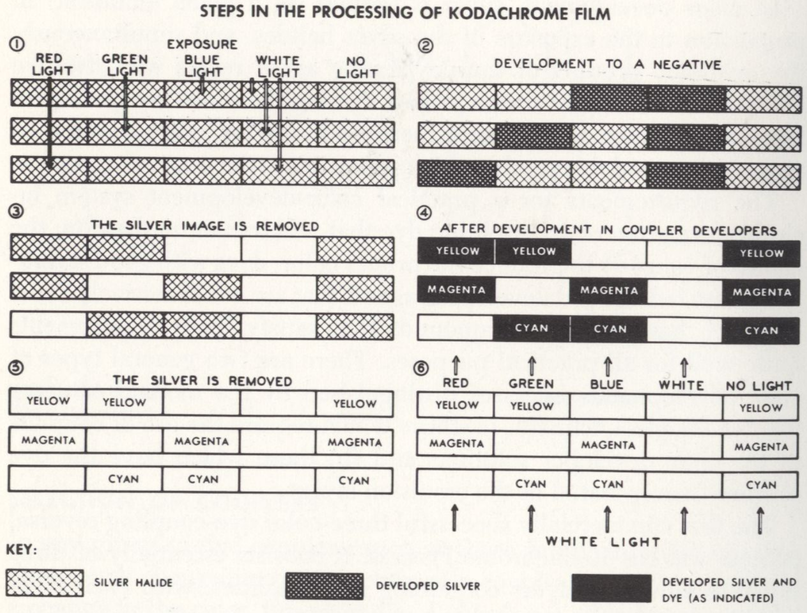

STEPS IN THE PROCESSING OF KODACHROME FILM
①
EXPOSURE
RED LIGHT
GREEN LIGHT
BLUE LIGHT
WHITE LIGHT
NO LIGHT
②
DEVELOPMENT TO A NEGATIVE
③
THE SILVER IMAGE IS REMOVED
④
AFTER DEVELOPMENT IN COUPLER DEVELOPERS
YELLOW
MAGENTA
CYAN
⑤
THE SILVER IS REMOVED
⑥
RED
GREEN
BLUE
WHITE
NO LIGHT
WHITE LIGHT
KEY:
SILVER HALIDE
DEVELOPED SILVER
DEVELOPED SILVER AND DYE (AS INDICATED)

FIGURE 5 The Kodachrome process

COMPOSITION OF COLOR DEVELOPERS

In general, color-forming developers are quite similar in composition to the conventional black-and-white developers in that they contain the same basic ingredients of developing agent, activator, preservative, and restrainer. However, the proportions of the various ingredients are quite different, and some of the ingredients, such as the color-developing agent, are much more complicated compounds. Also, the color developer usually contains additional special ingredients, even when the dye coupler is incorporated in the emulsion.

This can be illustrated by comparing the typical black-and-white developer formula on page 36 (Kodak Developer D-72) and the following typical color developer which is used with couplers incorporated in the emulsions.

Color Developer (Kodak SD-35)

Water, 70 to 80F (21 to 27C)	1.0	liter
Benzyl Alcohol	6.0	cc
Stir about 5 minutes to insure complete solution.		
Sodium Hexametaphosphate or Calgon	2.0	grams
Kodak Sodium Sulfite, desiccated	5.0	grams
Trisodium Phosphate · $12H_2O$	40.0	grams
Kodak Potassium Bromide	0.25	gram
0.1% solution of Kodak Potassium Iodide	10.0	cc
Kodak Sodium Hydroxide	6.5	grams
Kodak Color Developing Agent, CD-3 4-amino-N-ethyl-N-(β-methane-sulfonamidoethyl)-m-toluidine sesquisulfate monohydrate	11.33	grams
Ethylenediamine Sulfate	7.8	grams
Citrazinic Acid (2,6-Dihydroxy-isonicotinic acid)	1.5	grams

Developing Agent. Special developing agents are required for color processing to produce oxidation products that react with the incorporated couplers to form the dye images.

Frequently, they require a "booster" in addition to the alkali activators in the formula, and benzyl alcohol is added for this purpose. It is an organic solvent and, as such, probably accelerates the penetration of the developing agent into the different layers of the color material. The concentration must be carefully controlled because too much or too little benzyl alcohol can affect the sensitometric characteristics of the image. Some of the silver halide solvent, ethylenediamine sulfate, is also used.

Activator. For this purpose two alkalies are used, trisodium phosphate and sodium hydroxide. These are stronger alkalies than sodium carbonate and are used both to provide a higher pH for this developer and to buffer the solution to increase its capacity to neutralize acid by-products of the development reaction, as well as to insure the solubility of the developing agent.

Preservative. Although the same preservative, sodium sulfite, is used, the concentration is very much lower than in the black-and-white developers. In color development, the oxidation products of the developing agent must be free to react with the coupler for dye formation. A high concentration of sulfite would prevent this. On the other hand, some preservative is required to minimize aerial oxidation and to react with the unused oxidation by-products and prevent stains in the processed film.

Restrainer. Potassium bromide is used, but in considerably lower concentration and in combination with potassium iodide in the correct proportion.

Auxiliary Coupler. It is difficult in most color processes to obtain good control over contrast. Adjustments in the concentration of other constituents, such as activator, developing agent, etc, usually affect emulsion speed. However, a special compound like citrazinic acid can be added to the color developer to react with some of the oxidation products of the developing agent to form colorless compounds. This mechanism makes it possible to control the relation between the amounts of silver and of dye formed in the image, and thus control the contrast of the color image.

CHAPTE

9

The Measurement of Development

Up to this point photographic developers have been considered with respect to the action of the developer, the composition of developers, the mixing of developers, and the chemistry of development. In the practical use of developers, measurement of the degree of development is important. It is therefore discussed here.

• In order to understand clearly the effects of various factors in development, some means of measuring the image silver formed during development is required. The measurement of development effects is a part of "sensitometry." As early as 1890, Hurter and Driffield studied the relationship between the exposure and the amount of silver formed during development.

Light was passed through the silver image, and a measurement of the fraction of the light getting through was used as an indication of the amount of silver formed in the image. This fraction usually expressed in percent, is known as the "transmission." However, the transmission decreases as the image blackness, or amount of silver, increases. It would be more descriptive to use the "opacity," which is the inverse of the transmission, and thus increases with increasing silver.

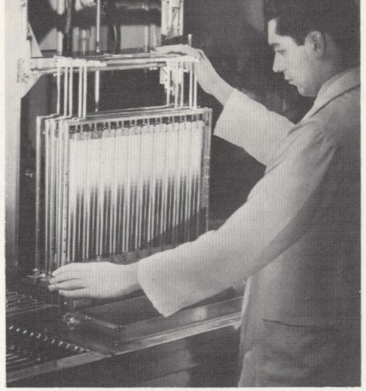
Hurter and Driffield found that, for a number of reasons, it is more meaningful to use the logarithm of the opacity, or "density," instead of the arithmetic value of opacity. For one thing, the human eye judges tone differences, or brightness differences, in logarithmic terms. For another, because of the way in which an image absorbs or stops the light, it was found that, for any given emulsion type, the amount of silver in the image is almost directly proportional to the density.

Mathematically, these relations can be expressed as follows:

$$\text{Transmission (T)} \quad \frac{\text{light striking the image}}{\text{light passing through the image}},$$

$$\text{Opacity (O)} = \frac{1}{\text{Transmission}} = \frac{\text{light striking the image}}{\text{light passing through the image}}, \text{ and}$$

$$\text{Density} = \text{logarithm of opacity} = \log \text{O}.$$

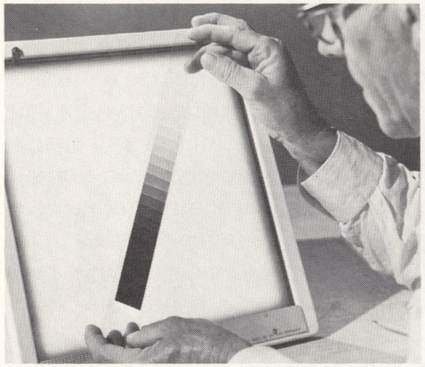


Above — Test samples of the material are exposed in a sensitometer like this one.

Above right — The sample receives uniform mechanical agitation during processing.

Below — The processed test sample.

Below right — A recording densitometer measures and plots the densities of the test sample.



Sensitometric testing of photographic materials during manufacture.

Processing. This cycle of operations, particularly the development, must also be accurately duplicated. It is important to control the composition of the processing solutions, the time, the temperature, and the amount of agitation. For the routine testing of sensitized materials the developers and fixing baths are mixed in large volumes so that the same solutions are available over considerable periods of time. It is not unusual in very extensive sensitometric testing operations to mix and store processing solutions in 500-gallon volumes. The storage tanks are usually located at a level above the testing stations to permit gravity flow as required.

Since temperature of the solution is difficult to adjust and duplicate just before each test, it is customary to keep the storage tanks submerged in a water bath adjusted to 68 F, the processing temperature considered as standard by the American Standards Association, Inc. Similarly, the processing tanks are also submerged in water baths kept at 68 F.

Agitation is probably the most difficult factor to control. The oxidation products of the developing agent and the alkali halides which are formed during the development reaction can interfere with development. Generally, when no agitation is employed, these by-products accumulate at the emulsion surface and within the emulsion, thereby slowing down the development. Agitation should therefore be uniform and sufficiently vigorous to remove the by-products of development and allow fresh developer to reach the emulsion continuously throughout the development time. Efficient agitation is also required in the rinse bath, in the fixing bath, and during washing.

Therefore, special agitation devices have been designed to accomplish this difficult operation. One system used at the present time for processing sensitometric tests consists of moving vertical blades placed approximately at right angles very close to the emulsion surface. The blades and test samples are immersed completely in the solution and the blades are moved automatically from side to side. In effect, the blades "wipe" the emulsion surface, causing the partially used developer to be brushed away from the surface and fresh developer to flow into contact with the surface. The speed of this operation is adjusted to provide uniform development.

Densitometer. This is an optical instrument designed to measure accurately the optical density of the developed photographic image. In routine sensitometry, it is used primarily for measuring the densities of the reproductions of the standard step tablet. In practical photography, it can be used to read the densities in negatives in those applications where accurate control of processing is required.

VALUE OF SENSITOMETRY

For many years the importance of controlled exposure and processing was realized. However, it was difficult to determine accurately the true effects of all the factors involved. The development of the techniques described above made this possible. For example, under these controlled test conditions, one factor, such as the emulsion, can be changed, and since all of the other factors are controlled and reproducible, the characteristics of the new emulsion can be compared to those of any other emulsion processed under the same conditions. Similarly, the effects of temperature, agitation, developer composition, etc, can be studied individually so long as all of the other factors

Negative-Positive Systems: Kodak Ektacolor Films (in sheets) and Kodacolor Film (in rolls) produce color negatives, from which color prints can be obtained on Kodak Color Print Material, Type C or color transparencies on Kodak Ektacolor Print Film. All of these materials require color development, and they have the dye couplers incorporated into their emulsion layers. The essential steps in the processing of these materials include: development of the exposed silver halides to form silver images and, simultaneously, the dye images in the three emulsion layers; bleaching of the silver in a special bleach bath; and removal of both the unused original silver halides and the bleached negative image in a fixing bath. Certain other supplementary treatments and, of course, rinses or washes between the various steps are also needed.

Outlines of the actual processing steps are shown in the following table.

TABLE V

Kodak Color Process C-22 Kodak Ektacolor Film, Type S Kodak Ektacolor Print Film Kodacolor Film	*Kodak Color Process B-41* Kodak Ektacolor Film, Type B Kodak Ektacolor Print Film	*Kodak Color Print Process P-122* Kodak Color Print Material, Type C
1. Developer	1. Developer	1. Developer
2. Stop Bath	2. Stop Bath	2. Stop Bath
3. Hardener	3. Hardener	3. Fixer
4. Wash	4. Wash	4. Wash
5. Bleach	5. Bleach	5. Bleach
6. Wash	6. Wash	6. Wash
7. Fixer	7. Fixer	7. Hardener Fixing Bath
8. Wash	8. Wash	8. Wash
9. Remove water droplets by wiping or with Kodak Photo-Flo Solution	9. Bathe in Kodak Photo-Flo Solution plus ¾ oz. Kodak Formaldehyde per gal.	9. Hardener
10. Dry	10. Dry	10. Wash
		11. Buffer
		12. Dry

Reversal Processes. The Kodak Ektachrome Processes E-1 and E-2, for color transparencies, and Kodak Color Print Process P-111, follow the general pattern for reversal processing, but they differ in a number of details. The basic steps include: reduction to silver, in the first developer, of the silver halides exposed in the camera or printer; exposure of the remaining undeveloped silver halides; development in the color developer to form the proper quantities of the three dyes; bleaching of the developed silver back to silver bromide; and removal of the silver bromide in a fixing bath. The various additional steps needed in the practical processes, such as stop bath, hardeners, and the various rinses and washes, are shown in the following table. It will be seen that there are some differences in the order of the steps between the Color Print Process, P-111, and the Ektachrome Processes. One important difference is in the point at which the reversal exposure is given. In the Ektachrome Processes, the films must be

TABLE VI

Kodak Ektachrome Process E-1	*Kodak Ektachrome Process E-2*	*Kodak Color Print Process P-111*
1. First Developer	1. First Developer	1. Prewet
2. Rinse	2. Rinse	2. First Developer
3. Hardener	3. Hardener	3. First Stop Bath
4. Reversal Exposure	4. Reversal Exposure	4. Wash
5. Wash	5. Wash	5. Reversal Exposure
6. Color Developer	6. Color Developer	6. Color Developer
7. Wash	7. Wash	7. Hardener Stop Bath
8. Clear	8. Clear	8. Wash
9. Rinse	9. Rinse	9. Bleach
10. Bleach	10. Bleach	10. Wash
11. Rinse	11. Rinse	11. Hardener Fixing Bath
12. Fix	12. Fix	12. Wash
13. Wash	13. Wash	13. Stabilizing Bath
14. Remove water droplets by wiping or with Kodak Photo-Flo Solution	14. Stabilizing Bath	14. Rinse
15. Dry	15. Dry	15. Dry

APPENDIX

1

Principles of Color Processes

Compared to black-and-white films, the sensitized materials used in three-color photography are complex. The basic principles of color photography are common to most of the current color processes.

• The principles of three-color photography have been described in detail in many treatises. However, a brief outline of these principles should serve to emphasize the complexities in color processing that do not exist in black-and-white photography, whether the process is based on negative-positive or reversal processing. It is helpful to understand the structure of color materials and to know how color processing is related to the exposure of the film.

It was pointed out in Chapter IV that the visible spectrum can be divided into three color regions – blue, green, and red – by the use of blue, green, and red filters, respectively. Each filter transmits its own color and absorbs the remaining colors. Similarly, when a colored object, illuminated with white light, is photographed on black-and-white film through a filter placed on the camera lens, the filter transmits its own color and absorbs the remaining colors. If the filter is blue, the film records the blue color of the object (Figure 18), but none of the other colors of that object. Therefore, with panchromatic-sensitized silver halide emulsions and the three color-separation filters, it is possible to obtain separate camera-film records of the blue, green, and red color components of an object. These are records of the *primary* colors of the object.

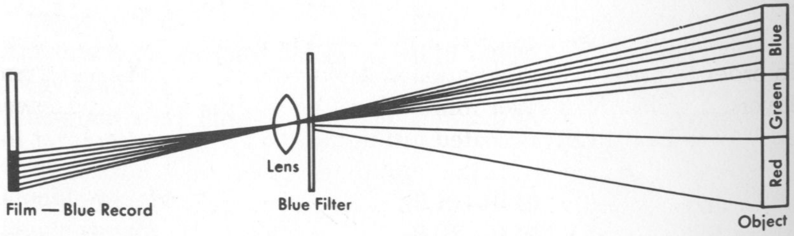


FIGURE 18

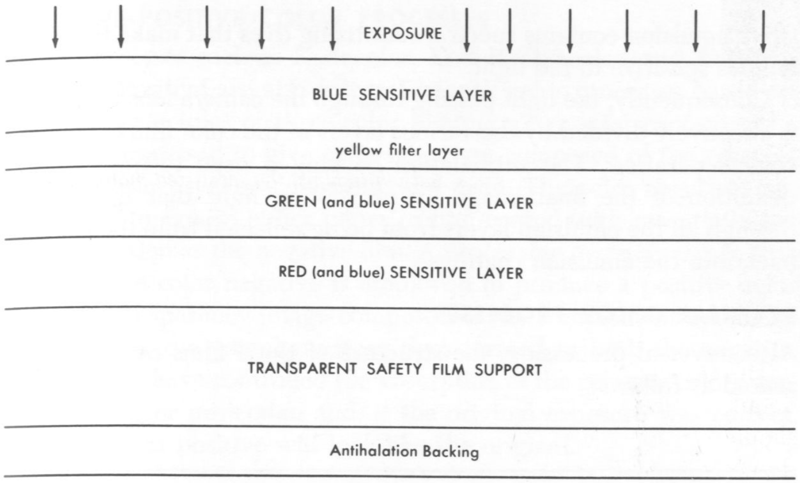

EXPOSURE
BLUE SENSITIVE LAYER
yellow filter layer
GREEN (and blue) SENSITIVE LAYER
RED (and blue) SENSITIVE LAYER
TRANSPARENT SAFETY FILM SUPPORT
Antihalation Backing

FIGURE 19 The structure of color film

In practical photography, it is impossible to make three color separations – one on each of three sheets of film – of moving or changing subjects unless quite complex and expensive camera equipment is employed. Even so, the three black-and-white separation records must then be converted into a color print, which requires considerable equipment, time, and experience. Fortunately, it has been possible to manufacture special color films that can record the separate colors simultaneously and then be processed to provide the final transparency. These products are known as *integral tripack color films*, examples of which are Kodachrome Film, Kodak Ektachrome Film, and Kodak Ektacolor Film.

Figure 19 illustrates the physical structure of this type of color film. During exposure the light strikes the blue-sensitive layer first, and a record of the blue component of the object is obtained. This emulsion is sensitive to blue light only and does not respond to green or red. Therefore, only a blue record is obtained. However, the silver halides in all of the emulsion layers are sensitive to blue light, and in order to prevent the formation of a blue record in the two bottom layers, a yellow filter layer formed from finely divided silver, known as "Carey-Lea silver," is coated just under the blue-sensitive layer to absorb all of the blue from the light passing through it.

The green-sensitive emulsion contains spectral sensitizing dyes that make the silver halides sensitive to green light but not to red light which is transmitted through this layer to the next one. The red-sensitive emulsion contains spectral sensitizing dyes that make the silver halides sensitive to red light.

Consequently, the light passing through the camera lens to the film is effectively divided by the various layers of the color film to provide color separation. The antihalation backing is used to improve the definition of the final image by preventing light that has passed through all the emulsion layers from being reflected from the support back into the emulsion coatings.

REVERSAL COLOR PROCESSES

After reversal processing, the structure of these films can be represented as follows:

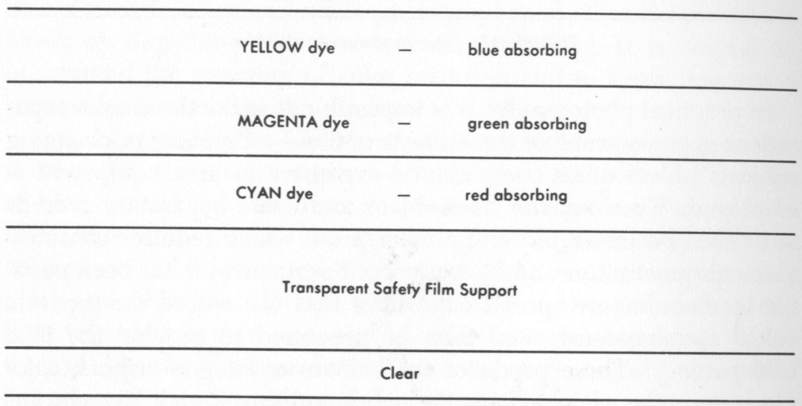

YELLOW dye — blue absorbing
MAGENTA dye — green absorbing
CYAN dye — red absorbing
Transparent Safety Film Support
Clear

FIGURE 20 Processed color film

Why are yellow, magenta, and cyan dyes formed during processing? Two important facts should be remembered in order to understand these color processes: (1) the original exposure provided records of the blue, green, and red components of the colored object, and (2) the final color transparency or print is viewed in white light and, to look like the original subject, should permit just the right amount of blue, green, and red colors to reach the eye. This control is obtained by forming during processing the complementary colors of blue, green, and red – yellow, magenta, and cyan, respectively. Thus, the yellow absorbs blue in those areas where the subject did not reflect blue, the magenta absorbs green where there was no green, and the cyan absorbs red where there was no red.

NEGATIVE-POSITIVE COLOR PROCESSES

Color processes such as Kodacolor, Kodak Ektacolor, and Eastman Negative-Positive are also integral tripack color processes based on the same principles of three-color photography. After exposure, the films are processed to give color negatives composed of the complementary colors, yellow, magenta, and cyan. The color negatives are then used to expose either paper or film coated with essentially the same emulsion as the negative film. A processing cycle similar to that used for the color negative is employed to produce a positive color print or transparency image composed of the complementary colors.

Therefore, the complementary dyes formed in both the negative and positive have controlled the absorption of the primary colors during viewing or projection and, if the original exposure was correct, the final color positive will look like the original.